NMR Quantum Logic Gates for Homonuclear Spin Systems.

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Abstract

If NMR systems are to be used as practical quantum computers, the number of coupled spins will need to be so large that it is not feasible to rely on purely heteronuclear spin systems. The implementation of a quantum logic gate imposes certain constraints on the motion of those spins not directly involved in that gate, the so-called "spectator" spins; they must be returned to their initial states at the end of the sequence. As a result, a homonuclear spin system where there is appreciable coupling between every pair of spins would seem to require a refocusing scheme that doubles in complexity and duration for every additional spectator spin. Fortunately, for the more realistic practical case where long-range spin-spin couplings can be neglected, simpler refocusing schemes can be devised where the overall duration of the sequence remains constant and the number of soft pulses increases only linearly with the number of spectator spins. These ideas are tested experimentally on a six qubit system: the six coupled protons of inosine.

1 Introduction

If a system of nuclear spins is to be of real practical use as an NMR quantum computer [1-13] it should consist of tens of coupled nuclei, otherwise the accessible algorithms will afford no real advantage over those that can be readily implemented on a classical electronic computer. Unfortunately the number of suitable (and non-radioactive) spin-1/2 nuclei is strictly limited; the prime candidates are ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si and ^{31}P, while chemical considerations appear to rule out the two noble gases ^{3}He and ^{129}Xe, together with most of the heavy metals. Consequently, an NMR quantum computer with a very large number of qubits is only likely to be attainable if it includes extensive homonuclear systems of coupled spins. These spins must all form part of the same molecule, consequently chemical bonding constraints favour the nuclei ^{1}H, ^{13}C, ^{19}F. Thus a key task is to understand how to perform a logic operation on a homonuclear system, for example an array of coupled ^{13}C spins. This is the difficult part of the problem, whether or not heteronuclear spins are also involved, and is the subject of this Letter.

A recent paper [12] has emphasized this new "do nothing" aspect of NMR quantum computation. For a total of N homonuclear spins, all coupled to each other, we select either one "active" spin to perform a rotation, or two "active" spins to evolve under their spin-spin coupling operator, leaving $N-1$ or $N-2$ "spectator" spins to be returned to their initial states at the end of the sequence. Because each logic gate has an appreciable duration, normally measured in tens of milliseconds, the "do nothing" feature is non-trivial, involving the refocusing of all chemical shift and spin-spin coupling interactions of the spectator spins, and the couplings between the active spin(s) and all the spectators.

A fundamental constraint is that no two coupled spins should experience simultaneous soft pulses. Although spin-spin coupling can be neglected during a short hard radiofrequency pulse, this is not the case for simultaneous pulses that are selective in the frequency domain. If the duration of the two soft pulses is comparable with the reciprocal of the coupling constant, undesirable antiphase magnetization and

multiple-quantum coherences are generated [14-17]. This so-called double-resonance two-spin effect "TSETSE" is irreversible and interferes with the proper operation of the logic gate. This constraint dictates the form of the refocusing pulse sequence, which can become highly complex for large numbers of spins if they are all coupled together with appreciable coupling constants [12]. The soft refocusing pulses eventually "collide" in the time domain, setting a lower limit on the duration of the logic gate. Higher applied magnetic fields mitigate the problem by increasing chemical shift differences and hence permitting shorter (less selective) soft pulses.

Two recent papers [18,19] describe pulse sequences that are more efficient in that the total number of π pulses does not increase exponentially with N for a fully-coupled system of N spins. In both reports the analogy with Hadamard matrices is stressed, since to refocus chemical shift or spin-spin interactions requires equal periods of "positive" and "negative" evolution under the I_z or $2I_zS_z$ operators, and the Hadamard matrices provide an elegant formulation of this requirement, suggesting the most efficient recursive expansion procedure. Unfortunately the proposed schemes involve several pairs of simultaneous π pulses and are therefore unsuitable for homonuclear systems.

In general the design of suitable homonuclear pulse sequences can be based on traditional NMR "refocusing" considerations, or more formally on patterns derived from the Hadamard matrices. We draw up a section of a conventional Hadamard matrix in which the rows represent the different spins (I, S, R, Q, etc.) while the columns indicate the sense of nuclear precession (+ or −) in the different time segments. Spin-spin coupling between any two representative spins is refocused if the corresponding rows are orthogonal, the characteristic property of a Hadamard matrix. Consequently, for a four spin system, the pattern:

$$\begin{array}{ll} I: & + \; + \; + \; + \\ S: & + \; + \; - \; - \\ R: & + \; - \; + \; - \\ Q: & + \; - \; - \; + \end{array} \tag{1}$$

using the 4×4 Hadamard matrix, will ensure that spin I evolves only according to its chemical shift, with no splittings due to S, R and Q, while S, R and Q have

chemical shifts and spin-spin splittings refocused.

However this matrix does not satisfy the constraint that no two soft π pulses are simultaneous. A possible pattern which does satisfy the constraint is as follows:

$$\begin{array}{ll} I: & + \; + \; + \; + \; + \; + \; + \; + \\ S: & + \; + \; + \; + \; - \; - \; - \; - \\ R: & + \; + \; - \; - \; - \; - \; + \; + \\ Q: & + \; - \; - \; + \; + \; - \; - \; + \end{array} \tag{2}$$

This matrix involves selecting four rows from the 8×8 Hadamard matrix. We see that one possible pattern of refocusing pulses forms a (1-2-4) cascade as illustrated in Fig. 1.

To take a concrete example, consider first of all the case of five homonuclear spins ($ISRQT$) all interacting with each other with appreciable coupling constants. Suppose we wish to construct a controlled-not (CNOT) gate, which is written in terms of product operators as

$$e^{-i\frac{\pi}{2}I_y}e^{-i\frac{\pi}{2}(I_z+S_z)}e^{+i\frac{\pi}{2}(2I_zS_z)}e^{+i\frac{\pi}{2}I_y} \tag{3}$$

where, by convention, the operators are set out in time-reversed order (and we have ignored an irrelevant overall phase). The key step is the evolution of the I and S spins under the spin-spin coupling operator $2I_zS_z$. The overall duration of this sequence is determined by the "antiphase" condition:

$$\tau = (2n+1)/(2J_{IS}) \tag{4}$$

where n is an integer, normally zero. For the case of the CNOT as set out in (3), n should be even. The R, Q, and T spectator spins must be returned to their initial states at the end of the sequence. Refocusing of the appropriate chemical shifts and spin-spin interactions is achieved by two hard π pulses and the (1-2-4) cascades of selective π pulses shown in Fig. 1. Each spin experiences an even number of π pulses, and the soft π pulses are never applied simultaneously.

The extension to further coupled nuclear spins is straightforward but daunting. Additional stages are added to the cascades, and each new stage doubles the number

of time segments and contains twice as many soft π pulses. Since these pulses have an appreciable duration, a point is eventually reached where the overall length of the sequence has to be increased to accommodate so many soft pulses without overlap in the time domain. This would be implemented by increasing n in Eq. (4). Herein lies the principal drawback of the method, for a long sequence would be subject to appreciable decoherence effects. The onset of this condition is determined by the chemical shift dispersion of the nucleus under investigation at the field strength of the spectrometer. This favours ^{13}C or ^{19}F nuclei in the highest possible field, because this permits the shortest soft π pulses.

Fortunately in practice spin-spin couplings are relatively local, and in a large spin system many of the longer-range interactions are vanishingly small. This puts a quite different complexion on the "do nothing" feature. One can then find pulse patterns for the logic gate that do not incur an exponential increase in the number of pulses required as the number of spins is increased.

Consider the practical case of a system of spins disposed along a "straight" chain (no branching) where spin-spin couplings are limited to one-, two- and three-bond interactions, neglecting the rest on the grounds that they would be too weak to cause significant TSETSE effects. This would usually be a good approximation if we decide to study coupled ^{13}C spins in an isotopically enriched compound. For simplicity of illustration the active spins IS have been assumed to be at the end of the chain, but identical conclusions can be drawn for spins near the middle of a chain.

Simultaneous π pulses are now allowed, provided that the spins in question are separated by four or more chemical bonds, and provided that the two soft pulses are not too close in frequency [20]. This affords a dramatic simplification and there is no longer an exponential growth in complexity as more spins are added to the chain. Consider a chain of nine coupled spins ($ISRQTUVWX$). All the relevant splittings can be refocused by the application of repeated (1-2-4) cascades of soft π pulses separated by a stage where one spin (U in this case) has no soft π pulses at all (Fig. 2). This recursive expansion can be continued indefinitely without increasing

the number of time segments in the sequence beyond sixteen. Note that at no time are two soft π pulses applied simultaneously to spins less than four bonds apart, but that all shorter-range splittings are refocused. The number of soft pulses increases essentially linearly with the total number of spins, while the overall duration of the sequence remains constant.

The simplification can be taken one step further by neglecting all except one- and two-bond interactions. Then a sequence made up of only eight time segments suffices and (1-2) cascades can be employed (Fig. 3). Simultaneous soft π pulses are only applied to spins separated by at least three bonds, but all shorter-range interactions are refocused. Finally, in practical situations where all except the one-bond couplings can be neglected, an even simpler sequence of single soft π pulses can be used.

These ideas can be expressed in a slightly different form for coupled systems of protons or fluorine nuclei. The possible topologies comprise the two-bond geminal couplings, three-bond vicinal couplings, and the corresponding longer-range interactions. Since the coupling constants do not necessarily fall off monotonically with the number of intervening bonds, we consider them in order of decreasing magnitude, neglecting all those below a predetermined threshold, thus avoiding the awkward and unrealistic case where every spin interacts with every other with an appreciable coupling constant.

An experimental test of these proposals was carried out on six coupled protons in inosine (Fig. 4) dissolved in dimethylsulfoxide-d_6 containing some heavy water. The hydroxyl resonances were removed by exchange with deuterium. As before, the I and S spins were allowed to evolve under the scalar coupling operator, while R, Q, T, and U were passive spectators. A modified pulse sequence (the top six rows of Fig. 5) was used because it incorporates all the soft π pulses in pairs, an arrangement well known to compensate pulse imperfections [21]. The sign matrix corresponding to left-hand side of the sequence shown in Fig. 5 is not a Hadamard matrix but is constructed by repeating sections of a Hadamard matrix. The first six rows of the

sign matrix are

$$\begin{array}{lcccccccc} I: & + & + & + & + & + & + & + & + \\ S: & + & + & + & + & + & + & + & + \\ R: & + & - & - & - & - & + & + & + \\ Q: & + & + & + & - & - & - & - & + \\ T: & + & + & + & + & + & + & + & + \\ U: & + & - & - & - & - & + & + & + \end{array} \tag{5}$$

Note that no soft π pulses are applied to spin T; row T is therefore not orthogonal to rows I or S. This is allowed since we have assumed that J_{IT} and J_{ST} are negligible.

The sequence for a controlled-not gate, (3), employs evolution under the $2I_zS_z$ operator for a period $(2n+1)/(2J_{IS})$, giving a multiplet that is antiphase with respect to the J_{IS} splitting, but which requires a $\pi/2$ phase shift (the I_z and S_z terms) to convert from dispersion to absorption. Sequences are available [12] to implement the requisite z rotation while returning the spectator spins to their initial states. For the purposes of illustration we demonstrate only the evolution under the IS coupling, obtaining the phase shift by resetting the receiver reference phase when recording the I and S responses.

The soft pulse scheme set out in Fig. 5 is designed to refocus vicinal (three-bond) and long-range (four-bond) splittings. In practice only the vicinal couplings are well resolved for inosine in the rather viscous solvent.

The resulting spectra are shown in Fig. 6. The soft π pulses had a duration of 64 ms and were flanked by 1 ms delays, giving an overall duration of 528 ms for the sequence. The geminal coupling between I and S is 12.4 Hz, which requires $n = 6$ in Eq.(4) to achieve the antiphase condition while still accommodating all the soft π pulses. Although I and S show some effects of strong coupling (AB pattern) the antiphase condition is quite clear, while the four spectator spins have chemical shift and spin-spin couplings all refocused at the end of the sequence. This implements the key step of the controlled-not logic gate.

Systems with larger numbers of coupled spectator spins are readily handled by extending the pulse patterns of Figs. 2, 3 or 5, without increasing the overall duration of the sequence. The number of soft π pulses only increases linearly with

the number of spectator spins.

To summarise – there are not enough suitable spin-1/2 nuclear species to be able to construct an entirely heteronuclear NMR quantum computer with sufficient qubits to make it useful. Hence any viable device must contain extensive networks of coupled homonuclear spins, for example protons, fluorine or carbon-13. This imposes constraints which rule out some "efficient" schemes which are appropriate for heteronuclear systems [18,19] as the latter involve simultaneous soft pulses on pairs of coupled spins, a procedure well known to generate undesirable multi-spin coherences. We have demonstrated new sequences for the construction of a quantum logic gate with homonuclear spins, where the spectator spins undergo no net evolution for the duration of the gate. When applied to the most realistic case where each spin is coupled to a restricted set of neighbours (neglecting long-range couplings) they have the important feature that the total duration of the sequence does not increase as further spins are added to the system. Analogous considerations apply to systems made up of both homonuclear and heteronuclear spins; the latter are refocused with conventional hard π pulses of negligible duration. We show experimental results for a six qubit system: the six coupled protons in inosine.

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Figure Captions

Fig. 1. Refocusing scheme for a system of five homonuclear spins where each pair of spins has an appreciable spin-spin coupling. The ellipses represent frequency-selective inversion pulses. The active spins I and S evolve under the $2I_zS_z$ operator and the duration of the sequence is set to $\tau = 1/(2J_{IS})$. The spectator spins (R, Q, and T) are returned to their initial states at the end of the sequence. Note that the introduction of an additional spectator spin would necessitate a further stage of sixteen soft π pulses.

Fig. 2. Refocusing scheme for a chain of nine homonuclear spins for the case that spin-spin coupling over more than three chemical bonds can be neglected. I and S are the active spins evolving under the $2I_zS_z$ operator. The (1-2-4) cascade pattern would be repeated as more spectator spins are added. Consequently the complexity increases essentially linearly with the number of spectator spins.

Fig. 3. Refocusing scheme similar to that shown in Fig. 2, except that spin-spin coupling over more than two chemical bonds is neglected. The (1-2) cascade

pattern may be repeated indefinitely as more spectator spins are introduced without increasing the overall duration of the sequence.

Fig. 4. The six-spin system of inosine with active protons labelled I and S and the spectators R, Q, T and U.

Fig. 5. A refocusing scheme equivalent to that shown in Fig. 3 incorporating soft π pulses in pairs to compensate pulse imperfections. The first six rows of this sequence were used to obtain the experimental results shown in Fig. 6.

Fig. 6. (a) Part of the conventional 600 MHz spectrum of the six protons of inosine. (b) The spectrum obtained after the pulse sequences of Fig. 5, showing the I and S responses in antiphase dispersion with respect to $J_{IS} = 12.4Hz$. (c) Individual multiplets expanded in frequency 3.6 times, with a $\pi/2$ phase shift applied to I and S to restore the absorption mode. Note that the spectators (R, Q, T and U) are essentially unchanged at the end of the sequence, apart from some minor attentuation through spin-spin relaxation.